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Јелена Станковић Петровић, Гордана Пантелић

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RAPID LSC METHOD FOR DIRECT ALPHA/BETA MEASUREMENTS IN WATERS

Ivana STOJKOVIĆ¹, Nataša TODOROVIĆ², Jovana NIKOLOV² and Branislava TENJOVIĆ²

- 1) *University of Novi Sad, Faculty of Technical Sciences, Novi Sad, Serbia, ivana_st@uns.ac.rs*
- 2) *University of Novi Sad, Faculty of Sciences, Novi Sad, Serbia, natasa.todorovic@df.uns.ac.rs*

ABSTRACT

Monitoring of environmental samples, drinking and surface waters, is continuously carried out, demanding development of methods that are both reliable and accurate on one side, but as simple and fast as possible, on the other. Screening tests such as gross alpha/beta activity measurements in water samples are one liquid scintillation counting (LSC) technique widely used as an efficient tool for radiological assesment and estimation whether water sample needs further analysis or not. In this paper, establishment of rapid gross alpha/beta screening technique in waters has been presented, which assumes modification of conventional ASTM D 7283-06 method, since samples were directly mixed with liquid scintillation cocktail, without any sample pretreatment. Method's optimization involved sample-to-cocktail ratio determination based on the achieved detection limit and sample's quench level. Optimal value of Pulse Shape Analysis (PSA) discriminator that considerably improves performance of LSC technique through alpha/beta spectra separation during radiological quality measurements of drinking waters has also been investigated. Results of calibration experiments and method's validity measurements on spiked samples with ²⁴¹Am and ⁹⁰Sr/⁹⁰Y aqueous standards are presented. Achieved detection limits for t_b 300 minutes of counting are $MDA_\alpha=0.294(11) \text{ Bq l}^{-1}$ and $MDA_\beta=0.405(5) \text{ Bq l}^{-1}$, in alpha and beta window, respectively. Direct alpha/beta method provides deviations up to 40% from reference values, but it offers advantages over conventional alpha/beta measurements, it is ultra fast, simple and inexpensive test for efficient screening of water samples.

1. INTRODUCTION

Radiological characterization of natural water samples often comes down to cost-effective procedure – screening of all samples for the presence of gross activities, an estimation of the total activity of all alpha and high energy beta emitters [1]. This radiochemical composition analysis in environmental studies indicates whether water sample contains elevated levels of any radionuclide. The use of low-background liquid scintillation counting (LSC) techniques permits the simultaneous measurement of both alpha and beta emitters with efficiencies close to 100% [2].

ASTM D 7283-06 Standard Test Method [3] for gross alpha/beta activity monitoring in drinking waters recommends preparation of samples by slow evaporation to dryness and addition of nitric acid before mixing with scintillation cocktail and assumes that efficiency detection depends on dry weight of samples, which is an indication of quench level present in samples. The purpose of this paper is to present optimization of rapid direct LSC method for ultra fast gross alpha/beta screening test in waters, without

sample preparation, and to investigate its possibilities and limitations. Similar studies have been conducted and reported in literature [4-5].

2. EXPERIMENTAL

All the samples have been counted on Ultra Low Level Liquid Scintillation Spectrometer Wallac 1220 Quantulus, specifically designed for low level activity measurements, containing low background construction materials, an anticoincidence active and a passive shield. Optimization for best possible separation of alpha and beta spectra, thus generating two separated spectra, is regulated with Pulse Shape Analysis (PSA) circuit where user can change PSA discriminator setting. The spectra were acquired by WinQ and analyzed by Easy View software by Perkin Elmer.

All samples were previously acidified with HNO_3 (to assure $\text{pH} \leq 2$) and mixed with water-miscible Ultima Gold AB scintillation cocktail in 20 ml polyethylene vials (glass vials were not used, since they introduce higher background). Background samples contained distilled water. Standard radioactive sources (^{241}Am , $^{90}\text{Sr}/^{90}\text{Y}$) produced from Czech Metrology Institute, Inspectorate for Ionizing Radiation were used for preparation of calibration samples, $A(^{241}\text{Am})=37.57 \text{ Bq ml}^{-1}$ with combined standard uncertainty 0.2%, reference date 1/10/2013, $A(^{90}\text{Sr}/^{90}\text{Y})=38.18 \text{ Bq ml}^{-1}$ with combined standard uncertainty 0.5%, reference date 1/10/2013.

Quantulus 1220 also has a quench control parameter, the Spectral Quench Parameter of the External Standard (SQP[E]), which is the lowest channel below which 99.75% of the counts generated when the sample is irradiated with a ^{152}Eu source, included in the counter, are registered [6]. SQP(E) decrease indicates higher quench level in samples.

3. METHOD AND CALCULATIONS

Efficiency detection and misclassification parameters calculations, defined and presented in detail in ASTM D 7283-06 Standard Test Method [3], were based on the measurements of pure α and β emitters as well as the background samples - all prepared with the certain sample: scintillation cocktail volume ratio, without additional quench corrections. Since there is no dry weight of sample as ASTM method assumes, here in direct method, efficiency parameters of α -particles in α -ROI ($\epsilon_{\alpha\alpha}$)($\epsilon_{\alpha\alpha}$) and in β -ROI ($\epsilon_{\alpha\beta}$)($\epsilon_{\alpha\beta}$), efficiency detection parameters of β -particles in β -ROI ($\epsilon_{\beta\beta}$)($\epsilon_{\beta\beta}$) and in α -ROI ($\epsilon_{\beta\alpha}$)($\epsilon_{\beta\alpha}$), as well as misclassification factors, α -in- β ROI ($X_{\alpha}X_{\alpha}$) and β -in- α ROI ($X_{\beta}X_{\beta}$), were determined as constants for each sample: scintillation cocktail volume ratio. Calibration experiments were carried out on optimal PSA level values previously determined for each sample-to-cocktail ratio. ASTM method recommends that Minimal Detectable Activity, MDA_{α} [Bq l^{-1}] and MDA_{β} [Bq l^{-1}], in α -ROI and in β -ROI, respectively, should be determined for each of the measured samples. In direct method, MDA_{α} and MDA_{β} were evaluated for each of the investigated sample:cocktail ratios according to Currie expression [7], based only on background count rates in α -ROI and β -ROI.

4. RESULTS AND DISCUSSION

Optimal value of PSA discriminator, which can be set between 1-256 on Quantulus, was investigated for different sample: cocktail ratios to ensure accurate and reliable

alpha/beta spectra separation, as presented in Table 1. Average SQP(E) values were measured at first for active samples (^{241}Am or $^{90}\text{Sr}/^{90}\text{Y}$ spiked to distilled water), which indicate the manner in which quench level changes for different volume ratios: it gradually increases with sample volume. It is also interesting to observe SQP(E) parameter behaviour in blank samples prepared with scintillation cocktail in different volume ratios: its decrement is more rapid with increased blank sample volume than in case of active samples where ^{241}Am or $^{90}\text{Sr}/^{90}\text{Y}$ solutions are present.

Table 1. Optimal PSA determination and MDA dependence for different sample-to-cocktail ratios

Sample:cocktail volume ratio	Optimal PSA	Average SQP(E) of active samples	SQP(E) of blank sample	MDA_{α} [Bq l ⁻¹]	MDA_{β} [Bq l ⁻¹]
4:16	89	830 (9)	830	0.671(23)	1.098(12)
5:15	90	820 (7)	817	0.537(19)	0.849(10)
6:14	91	813 (11)	810	0.449(16)	0.718(8)
7:13	91	803 (13)	796	0.423(13)	0.650(7)
8:12	92	795 (8)	790	0.345(12)	0.542(6)
9:11	91	797 (9)	775	0.366(12)	0.474(5)
10:10	93	792 (9)	760	0.319(11)	0.438(5)
11:9	96	791 (10)	745	0.294(11)	0.405(5)
12:8	99	785 (11)	728	0.303(12)	0.417(5)
13:7	105	783 (12)	713	0.368(13)	0.419(5)
14:6	108	783 (16)	684	0.447(16)	0.442(5)
15:5	111	774 (11)	663	0.459(19)	0.481(6)
16:4	115	757 (10)	641	0.527(19)	0.483(6)

Table 1 provides results of optimal volume ratio investigation as well, where indications are based on the achieved detection limit and quench level of sample, with respect to the capacity of scintillation cocktail. It is clear that 11:9 is optimal sample-to-cocktail ratio with moderate quench level for which optimal PSA parameter is determined to be 96, whilst MDA 's are 0.294(11) Bq l⁻¹ for gross alpha activity, and 0.405(5) Bq l⁻¹ for gross beta activity for $t_b t_b = 300$ min. Longer counting time could further reduce obtained MDA values. Since recommended screening levels are set to 0.1 Bq l⁻¹ for gross alpha and 1 Bq l⁻¹ for gross beta activity by EURATOM [8], direct α/β method provides only a screening tool adequate in emergency situations. Obtained MDA 's are still below values recommended in official law of Republic of Serbia: 0.5 Bq l⁻¹ for gross alpha activity and 1 Bq l⁻¹ for gross beta activity [9], which makes direct α/β method suitable for drinking and surface waters monitoring in Serbia. If complete ASTM method is implemented, MDA parameters can be reduced about 20 times if the samples are evaporated to dryness before mixing with cocktail [10], which is time-consuming procedure, nevertheless.

Efficiency detection and misclassification parameters for all of the investigated volume ratios are provided in Table 2. Smaller sample volumes have higher efficiencies, but higher detection limits also. Misclassification factors, X_{α} and X_{β} , are gradually increasing, following the increment of quench level with sample volume (Table 1), as

expected. We conclude that ratio 11:9 is optimal in all investigated parameters with minimal detection limit achieved.

Table 2. Efficiency and misclassification parameters of different volume ratios

Sample:cocktail volume ratio	$\epsilon_{\alpha\alpha}$ $\epsilon_{\alpha\alpha}$ [%]	$\epsilon_{\alpha\beta}$ $\epsilon_{\alpha\beta}$ [%]	$\epsilon_{\beta\beta}$ $\epsilon_{\beta\beta}$ [%]	$\epsilon_{\beta\alpha}$ $\epsilon_{\beta\alpha}$ [%]	X_{α}	X_{β}
4:16	96.98 (23)	4.89 (5)	190.2 (10)	3.36 (6)	0.0505 (6)	0.0177 (3)
5:15	96.9 (3)	5.26 (5)	191.4 (10)	3.54 (3)	0.0543 (6)	0.01848 (18)
6:14	96.5 (3)	5.29 (4)	190.4 (10)	3.78 (6)	0.054 (4)	0.0199 (3)
7:13	95.9 (3)	5.26 (9)	183.5 (10)	3.911 (23)	0.0550 (10)	0.02131 (18)
8:12	94.26 (24)	5.472 (23)	189.4 (10)	4.83 (3)	0.0581 (3)	0.02552 (20)
9:11	86.12 (19)	5.57 (5)	190.7 (10)	6.82 (9)	0.0646 (6)	0.0358 (5)
10:10	81.53 (17)	5.04 (8)	180.2 (9)	7.48 (12)	0.0618 (10)	0.0414 (7)
11:9	72.43 (20)	4.84 (3)	173.9 (9)	8.02 (5)	0.0669 (5)	0.0461 (4)
12:8	64.40 (16)	4.12 (5)	158.1 (8)	5.40 (8)	0.0640 (8)	0.0341 (6)
13:7	54.33 (23)	3.703 (16)	137.6 (8)	5.97 (8)	0.0682 (4)	0.434 (6)
14:6	41.57 (15)	3.65 (3)	121.2 (6)	5.48 (4)	0.0877 (7)	0.0452 (4)
15:5	34.03 (13)	3.44 (3)	105.1 (7)	5.03 (7)	0.1010 (10)	0.0478 (7)
16:4	27.77 (6)	3.457 (12)	92.7 (5)	5.72 (13)	0.1245 (5)	0.0617 (15)

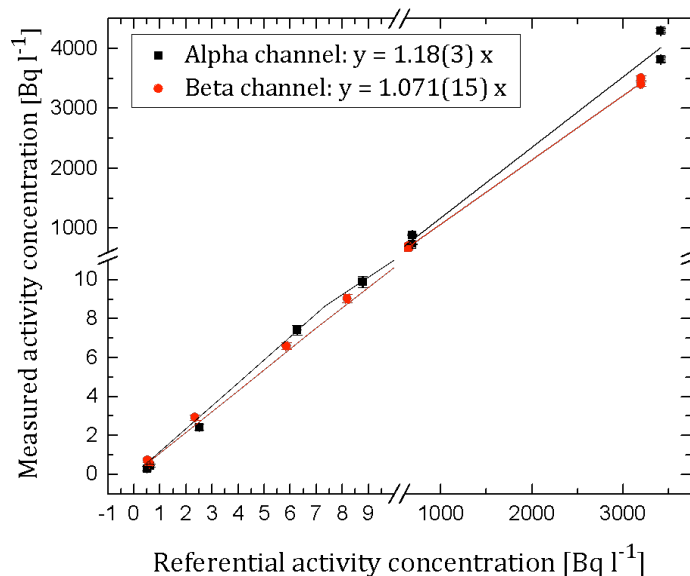


Figure 1. Method's validation measurements on spiked ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ samples

Method's accuracy and validity has been tested on spiked distilled water samples with $^{241}\text{Am}/^{90}\text{Sr}$ radionuclides in wide range of activities, as presented in Figure 1. Low $^{241}\text{Am}/^{90}\text{Sr}$ activity concentrations were selected from close to *MDA*'s to ~ 15 times higher than *MDA*'s in alpha and beta channel. On the other hand, samples with high activities had around 600 Bq l^{-1} and above 3000 Bq l^{-1} . All of them were prepared as typical environmental samples: $^{241}\text{Am}/^{90}\text{Sr}$ were spiked into 2 l plastic bottles with distilled water, acidified with HNO_3 and then prepared in 20 ml vials according to direct α/β method, 3 probes each and counted for a few 300 min cycles on Quantulus. Correlation coefficients were obtained as: 1.18(3) for alpha counts, and 1.071(15) for beta counts, which suggests that direct alpha/beta method tends to result in overestimated both alpha and beta activities, in general. For all of the spiked samples prepared, direct α/β method overestimated low activity concentrations up to $\sim 40\%$, both for alpha and for beta counts, whilst relative deviations for highly active samples were up to $\sim 30\%$ for alpha and $\sim 10\%$ for beta counts, respectively. It is important to mention that similar results were obtained for the same samples prepared and measured according to ASTM method also [11]. This indicates that both methods, direct and ASTM, do not provide exact measurements, but only screening tools for radioanalysis of environmental samples, most adequate in case of nuclear accidents and potential leakages monitoring from nuclear power plants. However, significant difference is that ASTM method provides up to 20 times lower detection limits, but extends preparation time of samples for at least two weeks.

5. CONCLUSIONS

Possibilities of rapid screening method development for gross alpha/beta measurements in waters have been presented. Samples have been directly mixed with liquid scintillation cocktail Ultima Gold AB, without any pretreatment i.e. without evaporation as conventional methods recommend. Calibration experiments have been prepared with ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ aqueous standards for different sample: cocktail ratios. Optimal ratio

has been established to 11:9 with $MDA_{\alpha}=0.294(11)$ Bq l⁻¹ and $MDA_{\beta}=0.405(5)$ Bq l⁻¹ for $t_b t_b=300$ min of counting on optimal level PSA=96. Presented radiological emergency procedure allows to obtain preliminary result whether the sample contains elevated levels of radioactivity in 5 hours.

6. ACKNOWLEDGEMENT

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DIREKTNA METODA ZA ODREĐIVANJE UKUPNE ALFA/BETA AKTIVNOSTI U VODAMA

**Ivana STOJKOVIĆ¹, Nataša TODOROVIĆ², Jovana NIKOLOV² i
Branislava TENJOVIĆ²**

- 1) Univerzitet u Novom Sadu, Fakultet Tehničkih Nauka, Novi Sad, Srbija,
ivana_st@uns.ac.rs
- 2) Univerzitet u Novom Sadu, Prirodno-matematički fakultet, Novi Sad, Srbija,
natasa.todorovic@df.uns.ac.rs

SADRŽAJ

Rutinski monitoring pijaćih i površinskih voda sprovodi se kontinuirano i nameće potrebu za razvojem metoda koje su, s jedne strane, pouzdane i tačne, ali istovremeno, jednostavne i brze. Screening testovi radi procene ukupne alfa/beta aktivnosti u uzorcima voda, jedna su od često primenjenih tehnika tačne scintilacione spektroskopije, kojima se efikasno može utvrditi da li uzorak zahteva dalju radiološku analizu ili ne. U radu je predstavljena optimizacija brze direktne metode za ispitivanje ukupne alfa/beta aktivnosti u vodama, uz prikaz i diskusiju postignutih granica detekcije. Ova metoda je modifikacija standardne test metode ASTM D 7283-06 za ispitivanje ukupne alfa i beta aktivnosti i podrazumeva direktno mešanje uzorka vode sa scintilacionim koktelom. Na taj način, uzorak je spreman za merenje bez prethodne pripreme koja, prema standardnim metodama, obično podrazumeva duge procedure poput uparavanja do suvog ostatka. Optimizacija metode sastoji se u određivanju optimalnog odnosa uzorak: scintilacioni koktel na osnovu granica detekcije (MDA) u alfa i beta kanalima, kao i nivoa prigušenja u uzorcima, uzimajući u obzir i maksimalni kapacitet određenog koktela. Podešena je vrednost PSA (Pulse Shape Analysis) diskriminatora u cilju optimalne separacije alfa i beta spektara i redukcije pozadinskih efekata. Kalibracija i validacija metode je izvršena standardnim referentnim materijalima, rastvorima ^{241}Am i $^{90}\text{Sr}/^{90}\text{Y}$. Utvrđeno je da za 300 minuta merenja tačnim scintilacionim brojačem, mogu se izmeriti koncentracije aktivnosti koje premašuju vrednosti $\text{MDA}_\alpha=0,294(11) \text{ Bq l}^{-1}$ i $\text{MDA}_\beta=0,405(5) \text{ Bq l}^{-1}$ u alfa i beta kanalima, respektivno. Rezultati validacije metode pokazuju da maksimalna relativna odstupanja mogu iznositi do 40%, što je prihvatljivo, uzimajući u obzir da metod nije predviđen za precizno merenje koncentracija aktivnosti pojedinih radionuklida, već za celokupnu procenu radiološke bezbednosti uzoraka voda.